

ENAMELS. COATINGS

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TECHNOLOGICAL SPECIFICS OF DEVITRIFIED COMPOSITE HEAT-RESISTANT COATINGS FOR NICHROME ALLOYS

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Compositions are developed, technological parameters are determined, and the main properties are investigated for devitrified glass composite heat-resistant coatings of the $R_xO - Al_2O_3 - SiO_2 - TiO_2$ system (R is Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+}) for Nichrome alloys.

An efficient method for protecting Nichrome alloys from high-temperature corrosion is application of glass ceramic coatings that are formed at a temperature significantly different from the service temperature of the Nichrome alloys. This is an important technological feature of such coatings, which are capable of forming a glass ceramic structure that improves the service parameters of the protective layer. The structure depends on the composition of the glass matrix and the composite as a whole, including adhesive oxides and high-melting fillers, and on the formation specifics of the coating and Nichrome – coating contact layer and their phase composition. Therefore, it is important to identify the optimum composition, structure, and properties of the coatings. An optimum coating should have certain mechanical and thermomechanical properties, in particular, high strength of adhesion to Nichrome and substantial operating life, determined by thermal stability and thermal resistance.

The glass matrix developed for protective coatings was based on the multicomponent system $R_xO - Al_2O_3 - SiO_2 - TiO_2$ (R is Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+}), and in addition to that, NiO , CoO , MnO_2 , and Fe_2O_3 were introduced. The firing regime for the coatings was set taking into account the dilatometric characteristics of the glass matrix and the temperature interval of Nichrome alloy service. The firing temperature for the coatings was selected in the interval of 900–1150°C, and the firing duration was in the interval of 3–6 min. It was found that the following firing regime was optimum for coating formation: temperature 1150°C and process duration 5 min.

In studying the strength of adhesion of the coatings to Nichrome alloys it was found that the lowest adhesive

strength was exhibited by coatings containing NiO , MnO_2 , and Fe_2O_3 . An increase in the MnO_2 content degrades the adhesive strength: when the MnO_2 content is increased from 1 to 8 weight parts, the amount of chips in the coating increases from 15 to 30%, and before Nichrome from 10 to 20%. The adhesive strength of the coatings to Nichrome Kh20N80 is shown in Table 1.

High adhesive strength is exhibited by coatings containing NiO , CoO , and Fe_2O_3 in the proportion $NiO : CoO : Fe_2O_3 = 8 : 1 : 1$. Coatings 1, 4, and 7 were selected for further investigation.

It is obvious that the Nichrome – coating contact layer has a substantial effect on the adhesion of the Nichrome substrate to the coating (the amount of chips in the coating is 1.5–2.1 times higher than before Nichrome is used).

TABLE 1

Coating	Proportion of oxides, weight parts, in coatings of series*			Adhesive strength, % chips per cm ²	
	I	II	III	in coating	before Nichrome
1	8 : 1 : 1	—	—	10	7
2	1 : 1 : 8	—	—	27	15
3	1 : 8 : 1	—	—	15	8
4	—	8 : 1 : 1	—	10	5
5	—	1 : 1 : 8	—	25	12
6	—	1 : 8 : 1	—	10	6
7	—	—	8 : 1 : 1	15	10
8	—	—	1 : 1 : 8	25	15
9	"	—	1 : 8 : 1	30	20

* I) $NiO : CoO : MnO_2$, II) $NiO : CoO : Fe_2O_3$, III) $NiO : MnO_2 : Fe_2O_3$.

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It is known that the adhesive strength and the operating life depend to a great extent on the conformity of the TCLE of the substrate and the coating. A study of the TCLE of the considered coatings revealed that the highest TCLE ($130 \times 10^{-7} \text{ K}^{-1}$) was exhibited by coating 4. The TCLE of this coating differs by $25 \times 10^{-7} \text{ K}^{-1}$ from the TCLE of Nichrome Kh20N80 used to make electric heaters for enamel-firing furnaces. This determined the high adhesive strength. Based on the results of the study of the adhesive strength and the TCLE, the optimum proportions of the oxide fillers for coatings 1 and 4 were determined (see Table 1).

It is known that it is primarily the thermal stability of the coatings that depends on their TCLE. Thermal-stability tests were conducted under severe conditions: after a hold for 3 min at 1000°C , the samples were abruptly cooled in water at room temperature until chips appeared. The indicated temperature was selected due to the fact that the initial coatings start to soften at a temperature above 1000°C . It was found that the highest thermal stability is exhibited by coating 4, which is characterized by absence of visible chips or stripes, a satisfactorily homogeneous surface, and a black luster. The thermal stability of coating 1 is significantly lower: needle-shaped chips appear after the first five thermal cycles, and the uniformity of the coating is broken. Coating 7 has unsatisfactory thermal stability.

Since the coatings are based on a glass matrix prone to devitrification, the relationship between thermal stability and heat-treatment temperature was analyzed. The heat-treatment temperatures were chosen on the basis of previously identified conditions for glass-matrix devitrification: $t_1 = 530^\circ\text{C}$ (the temperature at which recrystallization processes take place), $t_2 = 860^\circ\text{C}$ and $t_3 = 960^\circ\text{C}$ (the temperatures of formation of the main crystalline phases). The holding duration at each temperature was 2 h. After preliminary heat treatment the samples were subjected to thermal-stability tests. It was found that the thermal stability of the heat-treated samples is significantly higher than that of samples without heat treatment. Coating 4 has the highest thermal stability, which is 28 thermal cycles greater than that of coating 1 and 38 cycles greater than that of coating 7 (Fig. 1).

Taking into account the results of studying adhesive strength, TCLE, and thermal stability, coatings 1 and 4 were selected to investigate heat resistance. We investigated the

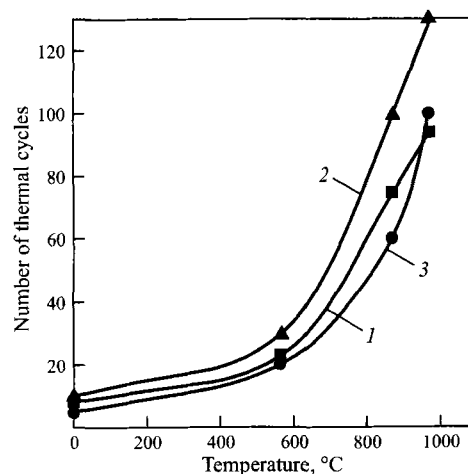


Fig. 1. Thermal stability of coatings 1 (1), 4 (2), and 7 (3) versus heat-treatment temperature.

heat resistance of Nichrome without a coating and with a coating (heat-treated and non-heat-treated). The heat resistance of the samples was inferred from the change in the sample weight in relation to the duration of holding at the same temperature, namely, 1000°C (Table 2).

The testing was carried out in several stages: 1000 h under laboratory conditions and under industrial conditions at the Lys'va Steel-and-Iron Works. The testing results were evaluated from the rate of gas corrosion calculated from the formula

$$K = m_0 - \frac{m}{S_0 \tau},$$

where m_0 is the initial weight of the sample, kg; m is the weight of the sample after testing, kg; S_0 is the surface area of the sample, m^2 ; τ is the testing duration, h.

The most significant changes in the sample weight under both laboratory and industrial conditions were recorded in the first 50 h of testing. In subsequent prolonged testing the weight increment became much smaller and stabilized at a certain level.

An analysis of the results showed that the coating, even when not subjected to heat treatment, protects nichrome Kh20N80 from oxidation. Thus, the weight change in sam-

TABLE 2

Sample	Change in sample weight, $\Delta m \times 10^{-3} \text{ kg/m}^2$, in time, h									
	5	10	15	20	25	30	35	40	45	50
Reference metal Kh20N80	2.00	2.30	2.70	3.50	3.60	3.60	3.70	3.70	3.71	3.71
Nichrome Kh20N80 with non-heat-treated coating:										
1	1.40	2.00	2.50	2.50	2.50	2.60	2.70	2.70	2.80	2.80
4	1.00	1.70	2.10	2.30	2.30	2.40	2.45	2.45	2.50	2.50
Nichrome Kh20N80 with heat-treated coating:										
1	0.40	0.70	1.60	1.70	1.70	1.70	1.80	1.80	1.80	1.80
4	0.20	0.40	1.40	1.40	1.50	1.50	1.50	1.60	1.60	1.60

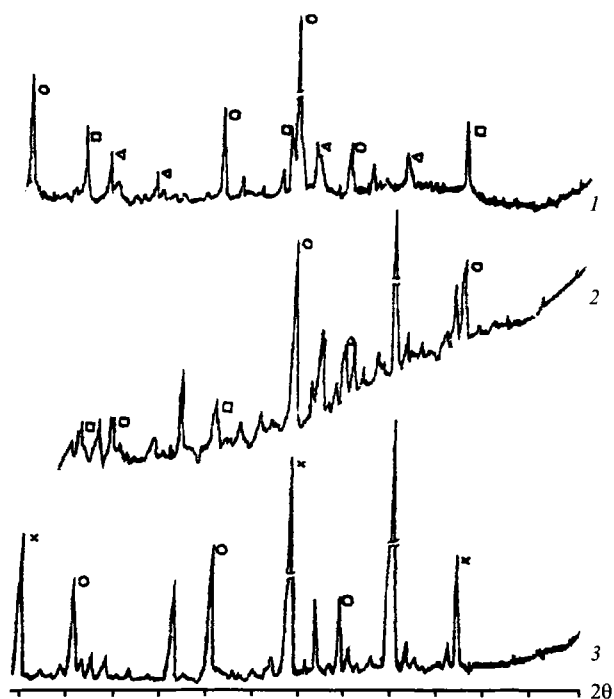


Fig. 2. X-ray patterns of coatings 4 (1), 1 (2), and the Nichrome – coating 4 contact layer (3): x) FeCr_2O_4 ; \square) FeAl_2O_4 ; \circ) NiFe_2O_4 ; Δ) Fe_2O_3 .

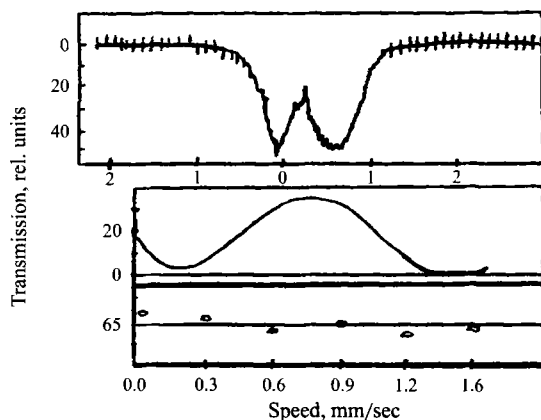


Fig. 3. NGR spectrum of a sample of Nichrome with coating 4 after prolonged testing.

ples with a non-heat-treated coating in the first hours of testing is less than the weight change in the reference sample: 1.43 times less for the sample with coating 1 and half as much for the sample with coating 4. An analysis of samples subjected to cyclic tests for 50 h revealed that coating 1 made corrosion 1.33 times weaker, and coating 4 made corrosion 1.48 times weaker. The results of heat treatment of Nichrome samples with coatings are as follows: after 5 h of testing the weight increment in the sample with coating 1 is reduced to one-fifth, and that of the sample with coating 4 to one-tenth,



Fig. 4. Surface of coating 4 after prolonged testing.

compared to the reference metal sample; after 50 h of testing the decrease is 2.06 and 2.32 times, respectively.

The combination of high levels of thermal stability, TCLE, adhesive strength, and heat resistance can be explained by studying the process of formation of a coating on a substrate. For this purpose, the phase composition and structure of the coatings and their contact layers with Nichrome were analyzed. The methods of analysis were x-ray phase analysis, nuclear gamma resonance spectroscopy (NGR spectroscopy), electron microscopy, and microspectral analysis.

The x-ray phase analysis of coatings 1 and 4 showed (Fig. 2) that coating 4 exhibits diffraction maxima relating to FeAl_2O_4 (0.160, 0.248, 0.479 nm) and NiFe_2O_4 (0.147, 0.208, 0.251, 0.294 nm). Furthermore, small quantities of hematite $\alpha\text{-Fe}_2\text{O}_3$ are identified (0.169, 0.184, 0.269, 0.368 nm). NiFe_2O_4 (0.254, 0.296, 0.488 nm) and FeAl_2O_4 (0.160, 0.169, 0.207 nm) were identified in coating 1. Apart from the revealed crystalline phases, the coating samples contain a vitreous phase. The x-ray phase analysis of the contact layer between Nichrome and coating 4 revealed differences in the phase composition of the coating and the Nichrome-coating composite. Thus, the contact layer contains the spinels NiFe_2O_4 (0.159, 0.208, 0.292 nm) and FeCr_2O_4 (0.146, 0.249, 0.477 nm) and crystalline silicate phases: gehlenite $\text{Ca}_2\text{Al}_2\text{SiO}_7$ and wollastonite CaSiO_3 (0.157, 0.162, 0.164, 0.176, 0.191, 0.239, 0.271, 0.327, and 0.457 nm).

The NGR-spectroscopic studies confirmed the presence of iron-bearing crystalline phases (Fig. 3) identified by the x-ray phase analysis. The stability of these phases in long service ensures a long operating life for the considered coatings.

The sample structure can be inferred from the results of the electron-microscopic studies, according to which the thickness of the contact layer of the Nichrome – coating 4 composite ranges from 10 to 40 μm (Fig. 4). The contact-layer material consists of particles of size 0.16 to 3 μm , which corroborates the presence of a devitrified structure in the Nichrome – coating system.

The performed physicochemical studies of the structure, phase composition, and properties of heat-resistant devitri-

fied coatings containing NiO , Cr_2O_3 , and Fe_2O_3 additives as adhesion activators suggest that chemical reactions between the Nichrome surface and the coating melt under conditions of high-temperature corrosion produce a devitrified structure that contains the indicated crystalline phases, including spinels and a residual vitreous phase.

It should be noted that nickel- and chromium-containing phases are stable in long service. The micro-x-ray spectral analysis of the characteristic radiation of nickel and chromium revealed that nickel in the metal is characterized by 1834 pulse/ m^2 , and chromium 711 pulse/ m^2 .

The Nichrome – coating 4 contact layer showed the following non-monotonicity of the change in the characteristic-radiation intensity of nickel and chromium: nickel – 29 pulse/ m^2 , chromium – 711 pulse/ m^2 . In our opinion, the micro-x-ray spectral analysis data indicate stability of chromium- and iron-containing phases in the course of long-time service of the coatings.

All this provides a long operating life for the coatings developed on the basis of the $\text{R}_x\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{TiO}_2$ system with NiO , CoO , and Fe_2O_3 additives.